(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 460 769 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
13.05.1998 Bulletin 1998/20

(51) Int. Cl.[6]: B01D 69/12, B01D 67/00

(21) Application number: 91201403.2

(22) Date of filing: 06.06.1991

(54) Semi-permeable composite membrane and process for manufacturing same

Halbdurchlässige zusammengesetzte Membran und Verfahren zu ihrer Herstellung

Membrane semi-perméable composite et son procédé de fabrication

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(30) Priority: 06.06.1990 NL 9001274

(43) Date of publication of application:
11.12.1991 Bulletin 1991/50

(73) Proprietor: X-Flow B.V.
NL-7612 AH Almelo (NL)

(72) Inventors:
- Koenhen, Dirk Marinus
NL-7701 RS Dedemsvaart (NL)
- Tinnemans, Aloysius Henricus Antonius
NL-3707 BG Zeist (NL)

(74) Representative:
Kupecz, Arpad et al
Octrooibureau Los en Stigter B.V.
Postbox 20052
1000 HB Amsterdam (NL)

(56) References cited:
EP-A- 0 046 136
EP-A- 0 174 045
EP-A- 0 227 043
US-A- 4 769 148
US-A- 4 802 984

- J. MACROMOL. SCI.-CHEM., vol A15, no. 5, 1981, pages 727-755, New York, US; J. E. CADOTTE et al.: "Interfacial synthesis in the preparation of reverse osmosis membranes"

Printed by Xerox (UK) Business Services
2.16.3/3.4

Description

The present invention relates to a semi-permeable composite membrane with a porous carrier substrate on which a polymer network obtained by interfacial polymerisation is applied, said network comprises an additional polymer and a process for manufacturing such semi-permeable membrane.

J. Macromolecular Science, vol.A15, no.5, 1981, pages 727-755 discloses semi-permeable composite membranes by means of an interfacial technique, however wherein merely reactive and ionic polymers are used as additives in order to improve the membrane properties such as the retention.

Such semi-permeable composite membrane is known from the European patent application 0 311 912. As porous carrier one uses herewith preferably a polysulphone. On the porous carrier polymeta-phenylene tetrahydrofuran 2,3,4,5-tetra-carboxamide is applied by interfacial polymerisation. Such membranes are suitable for use in aqueous systems, in particular for removing salts from aqueous solutions.

From the European patent application 0 275 027 is known that one may remove by reverse osmosis materials which are dissolved or dispersed in a solution or dispersing medium,wherein said materials are separated from the solvent respectively dispersing medium. The membranes used herein are selective permeable for certain components of the mixture to be separated. The known processes and membranes here described are particularly developed for separation processes in water. Herein an aqueous feed solution is brought in contact with a surface of the reverse osmosis membrane under pressure. The water permeability of the membrane is promoted by the applied pressure.

Membranes in general may be prepared from a polymer, for example polyamide, as described in the US patent 4,277,344. From more recent developments it has appeared that thin film composite membranes in particular are suitable for reverse osmosis. Such membranes which have a good salt retention are described in the US patents 4,520,044 and 4,606,943.

The US patent 4,769,148 describes thin film composite membranes for reverse osmosis which membranes are manufactured by interfacial polymerisation of a polyfunctional primarily water soluble primary or secondary amine in an aqueous solution with a relatively water insoluble polyfunctional acyl halide in an organic solvent.

Thin film composite membranes are in general prepared by interfacial polymerisation. Mostly one uses reactions of polyfunctional amines with polyfunctional acid halides or polyfunctional isocyanates.

In a known process a porous carrier substrate, in general a polysulphone ultra-filtration membrane is coated with a solution of one of the components whereafter the so coated membrane is brought in contact with a solution of the other reactive component wherein the respective solvents are inmiscible.

The reaction occurs at the interface wherein a thin polymer film with separation properties is obtained.

For ultra-filtration membranes in general the membranes are manufactured by the phase inversion technique. Such membranes may also be used as carrier substrates for the manufacture of thin film composite membranes.

Examples of such membranes are described in the US patents 3,926,798 and 4,039,440.

Sometimes one uses carrier substrates with big pores like microporous polypropylene (Celgard) and membranes prepared by the process of the US patent 4,798,847.

For gas separation processes there is a need for a separation layer which is as thin as possible. In general it is particularly difficult to directly obtain good results by the known processes in the manufacture of homopolymer membranes.

In this connection reference is made to the known US patent 4,230,463 wherein the membrane imperfections are blocked with a coating of polyphenyl methyl siloxane.

This process is used to approach as good as possible the intrinsic polymer separation properties.

Processes for the preparation of interfacial polymerisation composite membranes from siloxane polymers are described in the US patent 4,493,714.

These membranes primarily have the same properties as silicone membranes manufactured by solution deposit as described in the US patent 4,581,043 with this difference that possibly the thickness of the composite layer is thinner whereby productivity may be higher.

Increase of the separation factors for gas separation comprises the use of more densed polymer structures which may be obtained by treatment of the above-mentioned membranes by plasma coating as described in the US patent 2,191,502.

Composite membranes with a homogeneous coating are also used for reverse osmosis or ultra-filtration processes for th separation of solvents. A fluorine containing silicone coating is described in the US patent 4,748,288.

An example of such processes for the preparation of membranes for use in pervaporation may be found in the European patent application 0 312 378.

The use of homopolymers for membrane applications has various disadvantages.

In the first place, the choice of polymers is restricted in particular in the cases where the membrane is in contact with liquids like in reverse osmosis, ultra-filtration and pervaporation. The choice herein is restricted to polymers which do not dissolve or do not excessively swell in the disperging medium or which hav functional groups which are capable of causing cross-links.

So, for example, polyvinyl alcohol is only suitable as a pervaporation or reverse osmosis membrane for aqueous applications after a cross-links since otherwise the polymer would dissolve.

Another example is the use of polydimethyl siloxane as a membrane for removing lubricating oil (dewaxing) from a mixture of methyl ethyl ketone and toluene. Composite membranes with a polydimethyl siloxane coating show in such medium a too excessive swelling whereby they cannot be used. To avoid this problem one should, for example, use a fluorized siloxane polymer.

The use of interfacial polymerisation is also restricted since the used monomers or prepolymers always should contain polyfunctional reactive groups which may react at the interface.

The present invention aims to use a great number of polymers as membrane material, also in those cases where they cannot be provided with reactive groups or where they will swell excessively or dissolve in the dispersing medium respectively solvent with retainment of the possibility of obtaining thin membrane layers.

Herefor the present invention provides a semi-permeable composite membrane with a porous carrier substrate whereon a polymer network obtained by interfacial polymerisation is applied, said network comprises an additional polymer, characterized in that said additional polymer which is a non-reactive and non-ionic polymer is dissolved in the water phase or in the organic phase, from which said interfacial polymerisation occurs, which additional polymer is molecularly entangled in said network and influences in particular the selectivity and the permeability of the composite membrane.

The additional polymer present in the network may provide that the respective semi-permeable composite membrane, for example, has good fluxes since the said additional polymer shows a good solubility or swelling, which polymer usually would not be suitable for the manufacture of membranes. In the manufacture of the present membranes the additional present polymer is dissolved in one of the two solutions for the manufacture of the membrane by interfacial polymerisation.

Furthermore it is noted that surprisingly it has appeared that the first-mentioned additional polymer not only provides an instrument to influence the flux but also the retention which membrane properties are of great importance in the used separation processes.

The additional polymer present in the polymer network is a non-reactive polymer.

As non-reactive (and non-ionic) polymer one uses preferably polyalkyl siloxane either branched or not with the formula

$$-\left(\begin{array}{c} R \\ | \\ Si \\ | \\ R_1 \end{array} - O\right)_n-$$

wherein R and R_1 independent of each other represent a C_1-C_{20} alkyl or aryl group either substituted or not and n is an integral of 20-50.000 or a copolymer thereof.

The polyalkyl siloxane of the invention preferably is a polydimethyl siloxane with terminal trimethyl silyl groups.

In another favourable embodiment of the semi-permeable composite membrane of the invention the non-reactive polymer is a polyacrylate or polymethacrylate with the formula

$$-\left(CH_2 - \begin{array}{c} R_2 \\ | \\ C \\ | \\ C = O \\ | \\ OR_3 \end{array} -\right)_{\overline{n}},$$

wherein R_2 = H or CH_3 and R_3 is alkyl with 1-20 carbon atoms either branched or not, while n is an integral of ≥ 10.

Another favourable non-reactive (and non-ionic) polymer is a polyolefine either branched or not like for example polyisobutylene, polyisoprene or polybutadiene.

Further favourable non-reactive (and non-ionic) polymers are for example a block copolymer of styrene-butadiene-styrene, styrene-isoprene-styrene, styrene-ethylene-butylene etc.

Furthermore, according to the invention a cellulose acetate also appears to be favourable as non-reactive (and non-ionic) polymer in the scope of the invention.

Finally, it appears that a polyalkylene oxide, in particular polyethylene oxide with the formula $(CH_2\text{-}CH_2\text{-}O)_n$, wherein n is an integral of ≥ 20 gives good results when this non-reactive polymer is present in the semi-permeable composite membrane.

In general the polymer regulating the membrane properties is present in the polymer network in a quantity of 5-90%, by weight, and preferably in a quantity of 10-60%, by weight, related to the total weight of the network.

Finally, the invention comprises a process for the manufacture of a semi-permeable membrane by coating a porous substrate with a polymer network obtained by interfacial polymerisation, characterized in that the porous substrate is treated with a solution of at least a reactive polyfunctional monomer or oligomer or prepolymer with as reactive groups $-NHR_4$ (R_4 = H or alkyl with C_1-C_{20}), -OH or -SH and eventually a surfactant in water, whereafter the so treated substrate is further treated with a solution of at least one reactive polyfunctional monomer or oligomer or prepolymer or polymer with as reactive groups -COX, $-SO_2X$, $-POXR_5$, $-NR_6COX$ or -NCO, wherein X = Cl, Br or I, while R_5 and R_6 are an alkoxy group or alkyl group with 1-16 carbon atoms, preferably 1-5 carbon atoms in a suitable organic solvent wherein a non-reactive and non-ionic polymer regulating the membrane properties, prior to the treatment of the substrate with the aqueous solution of the said reactive components is added in an amount of 5 - 90%, by weight, and preferably in an amount of 10 - 60%, by weight, related to the total weight of the network to that solution in case the polymer is soluble in water, whereas in case the polymer dissolves in an organic solvent, this is added to the organic solution of the said reactive components whereafter the so treated substrate is dried and subsequently is or is not subjected to a heat treatment.

It is noted that in the preparation of the semi-permeable membrane of the invention the respective porous substrate is coated with a polymer network obtained by interfacial polymerisation starting from two phases, namely an organic phase with therein a reactive component as above-mentioned and an aqueous phase containing a water soluble reactive component which form after contacting each other a network. Prior to the interfacial polymerisation an additional polymer, usually a non-reactive polymer, is added to one of the phases which polymer is captured in the network obtained by interfacial polymerisation and cross-links.

The additional polymer, a non-reactive (and non-ionic) polymer, is insolubilized in the network wherein the swelling in the network is restricted to a value dictated by the network formed by the interfacial polymerisation reaction.

An additional advantage is that a particularly thin separation layer is formed which is difficult to obtain with other techniques like dip-coating or "kiss-roll"-coating. An eventual polymer surplus can be removed by washing with a suitable solvent, while a thin layer of the desired polymer remains entangled in the formed network.

In examining the reverse osmosis membranes for the separation of n-docosane from hexane, for example, it has appeared that when using a prepolymer of Polymeg (= poly(tetramethylene ether glycol)) with terminal isocyanate groups in the organic phase and an amine in a water phase under addition of a non-reactive polymer in the form of silicone to the organic phase the molecular weight of the Polymeg is of importance.

When using Polymeg with a molecular weight of 650 no flux could be observed, whereas the use of Polymeg with a molecular weight of 1.000 gave good results concerning the flux. When using Polymeg with a molecular weight of 2.000 very high fluxes were obtained but with a decrease of the retention.

From the foregoing it appears clearly that the density of the network wherein the silicone is captured is of importance. It is surprising that the fluxes strongly increase by adding siloxane in a dense network with retainment of the desired retention values.

However, when the network is too loose like for example with Polymeg 2.000 the silicone may swell too much thereby losing its performance.

When to a network built from an isocyanate terminated polydimethyl siloxane and a low molecular amine, which network has per se gas separation properties similar to normally used PDMS layers, an addition of poly(1-(trimethyl silyl)-1-propyne is done, it is observed that the gas permeability strongly increases whereas the separation factor decreases somewhat. Here the permeability primarily is determined by the added polymer showing a 10 x higher permeability in relation to a polymer known from the literature.

By the present cross-links process these membranes are also suitable for membrane application entirely or partially taking place in a liquid medium.

It has surprisingly appeared that by the present process various polymers may be used which otherwise are unsuitable for the manufacture of a membrane provided one combines these polymers with a membrane network obtained by interfacial polymerisation. The so formed effective layers are extremely thin in the order of magnitude of 0.05-0.5 µm, which membranes are particularly suitable for the manufacture of gas separation membranes.

It is noted that the present membranes are particularly suitable for various separation purposes like reverse osmosis, gas separation, separation of organic liquids and for separation aqueous solutions.

The following non-reactive (and non-ionic) polymers are suitable for use for reverse osmosis in aqueous systems:

- mixed cellulose esters like cellulose acetate butyrate (CAB), partially hydrolized CAB;
- ethyl cellulose.

The polymers are dissolved in the organic phase or the water phase. As long as the polymers satisfy this solubility requirement they may be used in principle.

For non-reactive polymers which are not soluble in solvents used in the interfacial polymerisation like aromatic polyamides, polypiperazine amides, polyhydrazides, polybenzimidazoles, etc. the possibility exists of still adding them by effecting such modification on the polymer that they show a suitable solubility in the organic phase or in the water phase.

The use of polymers in for example the water phase like for example for Nafion copolymers in an alcohol/water mixture also offers a possibility of introducing the polymer in the network obtained by interfacial polymerisation.

Examples of non-reactive polymers for reverse osmosis in non-aqueous systems are those already having a high affinity for the medium to be used in the reverse osmosis non-aqueous application:

- Elastomers with a high affinity relative to for example toluene like polyether urethanes, polyisobutylenes, polybutadienes, chlorinated polythenes, sulphonated polythenes, acrylic elastomers, polyepichlorhydrines, styrene butadiene rubber, butyl rubber, isoprene rubber, ethylene propylene rubber, neoprene rubber, chloroprene rubber, silicone rubber, urethane rubber;
- thermoplasts with a high affinity relative to for example toluene like polystyrene, chlorinated polyvinyl chloride;
- polymers with a high affinity for alcohols (methanol, ethanol, butanol); the polymers should be soluble in the water phase or in the organic phase, for example:
- poly-N-methyl-N-vinyl acetamide soluble in the water phase;
- poly(N,N-dimethyl acrylamide) soluble in methanol and with water at 40°C as water phase;
- poly(methyl tert-butyl fumarate) soluble in methanol and with benzene or chloroform as organic phase;
- poly(N-(1,1-dimethyl-3-oxobutyl)acrylamide) soluble in butanol and with toluene as organic phase;
- poly(isobutyl methacrylate) soluble in ethanol (hot) and in isopropanol above 23,7°C and with tetrachloro methane or n-hexane as organic phase.

When using the membranes for pervaporation purposes suitable polymers like polyurethane urea may be used as non-reactive polymer.

When using the membranes for gas separation gas separation properties of the added polymer may be called for, for example, supposing that the polymer is present as a thin separation layer, whereas the network polymer is badly permeable or impermeable for the gasses and is located in the separation layer or is located under the separation polymer layer and also is permeable for the gasses (not gas selective).

Also exists the possibility that the polymer hardly can form a solid aggregate state with own polymer chains but aggregate formation occurs with the polymer segments of the network.

Of certain elastomers it is difficult to obtain thin coating layers on microporous backgrounds by dip-coating. Baker et al. [J. Membrane Sci., 31 (1987) 259] state this for the elastomers: chloroprene, chloro sulphonated polythene (Hypalon) soluble in toluene, Fluorel, fluoro elastomer, polyacrylonitrile butadienes, silicone polycarbonate (General Electric Co.), e.g. "a sticky, rubbery material such as Hypalon is very difficult to manufacture into defect-free films.", page 270.

Trichloro ethane/N_2 or acetone/N_2 vapor mixtures lend themselves for separation with Hypalon. Addition of Hypalon to a polyurethane network perhaps leads to gas separation membranes therefor.

Under the term "retention" should be understood a value obtained by the following equation:

$$\text{Retention substance X (in \%)} = \left(1 - \frac{\text{concentration substance X in the permeate}}{\text{concentration substance X in the feed}}\right) \times 100$$

Under the term "flux" should be understood the quantity of permeate in liters passed by the membrane per m^2 during one hour at a certain working period.

The invention is further explained by the following non-limiting examples.

Example I

In a 1 liter round bottom provided with a distillation mount and a needle guide with a rubber septum were introduced 9.1 g (7.8 mmoles) of poly(tetramethylene ether glycol) (Polymeg 1000^{R}), Quaker Oats Co.; OH contents 1.73 mmoles/g) and 915 ml of toluene (pro analyse, Merck). From this solution under nitrogen atmosphere about 240 ml of

a mixture of toluene and water was removed by azeotropic distillation. Subsequently, the distillation mount was replaced by a reflux condenser while the solution remained under nitrogen atmosphere. To this solution were successively added by a syringe 2.75 g (15.8 mmoles) of toluene diisocyanate (T-80[R], Bayer), i.e. molar ratio Polymeg 1000/T-80 = 1/2 and 0.09 g of $[CH_3(CH_2)_{10}CO_2]_2\ Sn[(CH_2)_3CH_3]_2$ as catalyst. Subsequently, the reaction mixture was stirred during 3,5 hours at 65-70°C. The resulting yellow brown solution contained 2.0%, by weight, of prepolymer and a free toluene diisocyanate contents of about 15% (on the basis of GPC analysis after modification with di-n-butyl amine).

A wet flat support membrane of polyimide (0.35 x 0.12 m) prepared from a 16%, by weight, solution of a polyimide type (Lenzing P84) in DMF was applied to a cilindrical immersion body made of teflon. This support membrane was immersed during 15 minutes in a water phase with 1.0%, by weight, of NH_2-$CH_2CH_2CH_2$-NH-CH_2CH_2-NH-$CH_2CH_2CH_2$-NH_2, 0.05%, by weight, of poly(vinyl alcohol) (Mowiol 4-88[R], Hoechst) and 0.04%, by weight, of sodium dodecyl sulphate as surfactant. Subsequently, the membrane was removed from the water phase and the excess of aqueous solution at the lower side was removed with filtering paper. After a dripping period of about 7 minutes the membrane was transferred in an organic phase comprising toluene with therein dissolved 0.5%, by weight, of above-mentioned prepolymer and as additional non-reactive polymer 0.75 g of a poly(dimethyl siloxane) with terminal trimethyl silyl groups (Ak-Öl 100.000, Wacker Chemie) per gram prepolymer. The membrane was in the organic phase during 1 minute. Subsequently, the membrane was dried 5 minutes at room temperature and thereafter 15 minutes in an air circulation oven at 90°C. The obtained membrane contained a polymer network with therein entangled the non-reactive Ak-Öl.

The reverse osmosis properties of this membrane were determined at room temperature and at a pressure of 40 bar in a solution comprising n-hexane with therein dissolved 1.0%, by weight, of n-docosane (molar mass 310.6 dalton) with as result a n-hexane flux of 52 $l/m^2/h$ and a n-docosane retention of 73%.

Comparative Example IA

The procedure of example I was repeated on the understanding that the organic phase did not contain Ak-Öl. This membrane did not show a n-hexane flux in a reverse osmosis experiment as described in example I.

From the foregoing appears clearly the favourable effect of the non-reactive polymer Ak-Öl on the hexane flux and n-docosane retention.

Example II

In an analogous manner as described in example I a 3.26%, by weight, solution was prepared of a prepolymer prepared from toluene diisocyanate (T-80) and a polybutadiene with terminal hydroxyl groups (PBD 2000, Poly Sciences; OH contents 1.25 mmoles/g). Subsequently, in the manner described in example I a composite membrane was prepared. The water phase contained 0.5%, by weight, of the amine. The organic phase comprised toluene with therein dissolved 2.0%, by weight, of above-mentioned prepolymer on the basis of PBD 2000 and 0.75 g of Ak-Öl as non-reactive polymer per gram prepolymer.

The reverse osmosis properties of this membrane were determined at room temperature and at a pressure of 40 bar in a solution comprising toluene with therein dissolved 1.0%, by weight, of n-docosane with as result a toluene flux of 97 $l/m^2/h$ and a n-docosane retention of 53%.

Comparative Example IIA

The procedure of example II was repeated on the understanding that the organic phase did not contain Ak-Öl. This membrane did not show toluene flux in a reverse osmosis experiment as described in example II.

From examples II and IIA appears the favourable effect of the non-reactive polymer Ak-Öl on the toluene flux and n-docosane retention.

Example III

One proceeds in the manner described in example 1 in the preparation of a series of composite membranes (IIIa-IIId). The organic phase comprised toluene with therein dissolved 1.0%, by weight, of the prepolymer mentioned in example I and 0.75 g per gram prepolymer one of the non-reactive polyolefines mentioned in table A. The results of the flux and retention capabilities of a solution of 1.0%, by weight, of n-docosane in toluene at room temperature and at a pressure of 40 bar are mentioned in table A.

Comparative Example IIIA

The procedure of example III was repeated on the understanding that the organic phase only comprised 1.0%, by weight, of the prepolymer mentioned in example I. The results of the flux and retention measurements of a solution of 1.0%, by weight, of n-docosane in toluene and at room temperature at a pressure of 40 bar are mentioned in table A.

When comparing the results of example III and IIIA it appears that the non-reactive polymer namely polyolefine has a significant influence on the n-docosane retention and the toluene flux.

Example IV

In an analogous manner as described in example I a 3%, by weight, solution of a prepolymer was prepared from toluene diisocyanate (T-80) and polypropylene glycol (PPG 1000, Janssen Chimica, Belgium; OH contents 1.89 mmoles/g). Subsequently, in the manner described in example I a composite membrane was prepared. The organic phase comprised toluene with therein dissolved 1.0%, by weight, of above-mentioned prepolymer on the basis of PPG 1000 and as non-reactive polymer 0.75 g of Ak-Öl per gram prepolymer.

The reverse osmosis properties of this membrane were determined at room temperature and at a pressure of 40 bar in a solution comprising n-hexane with therein dissolved 1.0%, by weight, of n-docosane with as result a n-hexane flux of 123 l/m^2/h and a n-docosane retention of 73%.

Comparative Example IVA

The procedure of example IV was repeated on the understanding that the organic phase did not contain Ak-Öl. This membrane did not show a n-hexane flux in a reverse osmosis experiment as described in example IV.

The mentioned examples IV and IVA clearly demonstrate the influence of the non-reactive polymer on the n-hexane flux and n-docosane retention.

Example V

An isocyanate terminated prepolymer was prepared from hydroxyl terminated polymer-α,ω.bis(hydroxy propyl)polydimethyl siloxane in the manner described in examples I to IV.

In the usual manner a composite membrane was made on a suitable carrier.

To the organic phase in toluene was added as non-reactive polymer 1 g of fluoro silicone (Shin-Etsu X31-699) per gram prepolymer.

The water phase comprised 1%, by weight, of N4 (= N,N'-bis-(3-amino propyl ethylene diamine) with the usual additions.

As a control a membrane was made without the addition of fluoro silicones (comparative example VA).

Tests on a mixture of 33% spindle oil, 33% methyl ethyl ketone and 33% toluene gave the following results at a temperature of 25°C and a pressure of 40 bar:

	flux (l/m^2/h)	retention spindle oil
Example V	62.5	99.5%
Example VA	70	80 %

From this example it appears that by adding fluoro silicones as non-reactive polymer to the membrane the retention of spindle oil is 99.5% in relation to 80% without addition. The flux, however, is somewhat lower, namely 62.5 in relation to a membrane without addition, namely 70, but still sufficient for a justified operation.

Example VI

The procedure of example I was repeated on the understanding that the organic phase comprised toluene with therein dissolved 1.0%, by weight, of the prepolymer mentioned in example I and 0.75 g per gram prepolymer of a copolymer built from 80%, by weight, of isobutyl methacrylate and 20%, by weight, of methyl methacrylate. The results of the flux and retention measurements of a solution of 1.0%, by weight, of n-docosane in toluene at room temperature

and at a pressure of 40 bar are mentioned in table A.

Table A

Example	Additional non-reactive polymer 0.75 g/g prepolymer		Toluene flux $l/m^2/h$	Retention n-docosane
IIIA	none		204	60
IIIa	Oppanol B50	a)	73	85
IIIb	Cariflex TR 1101	b)	67	89
IIIc	Kraton G 1605	c)	31	91
IIId	Cariflex TR 1107	d)	68	84
VI	see example VI		24	88

a. Poly(isobutylene) M.W. = 400.000 (BASF)
b. Styrene-butadiene-styrene-block copolymer (Shell)
c. Styrene-ethylene/butylene-styrene-block copolymer (Shell)
d. Styrene-isoprene-styrene-block copolymer (Shell)

This example demonstrates the favourable effect of the non-reactive polymer on the retention of n-docosane at a decrease of the flux to a value which in economic aspect is totally acceptable.

Example VII

The procedure of example I was repeated on the understanding that the water phase contained 0.5%, by weight, of the amine. The organic phase comprised toluene with therein dissolved 1.0%, by weight, of the prepolymer mentioned in example I and as non-reactive polymer 0.75 g of poly(ethylene oxide), (M.W. 100.000, Aldrich) per gram prepolymer.

The reverse osmosis properties of this membrane were determined at room temperature and at a pressure of 40 bar in an aqueous solution with 1.0%, by weight, of sucrose with as result a water flux of 24 $kg/m^2/h$ and a sucrose retention of 60%.

Example VIII

The procedure of example I was repeated. The water phase comprised besides 0.5%, by weight, of NH_2-$CH_2CH_2CH_2$-NH-CH_2CH_2-NH-$CH_2CH_2CH_2$-NH_2, 0.05%, by weight, of poly(vinyl alcohol) (Mowiol 4-88^R, Hoechst) and 0.04%, by weight, of sodium dodecyl sulphate as surfactant. As non-reactive polymer 0.75 g of cellulose acetate per gram used prepolymer was added to the organic phase. The organic phase comprised toluene and dissolved therein 0.5%, by weight, of the prepolymer mentioned in example I.

The reverse osmosis properties of this membrane were determined at room temperature and a pressure of 40 bar in an aqueous solution with 0.1%, by weight, of NaCl with as result a water flux of 15 $kg/m^2/h$ and a NaCl retention of 80%.

Comparative Example VIIIA

The procedure of example VIII was followed on the understanding that no cellulose acetate was used. This membrane did not show water flux in a reverse osmosis experiment as described in example VIII.

Example IX

The procedure of example I was followed in the preparation of a series of composite membranes (IXa-IXc). The organic phase comprised toluene with therein dissolved 1.0%, by weight, of the prepolymer mentioned in example I and as non-reactive polymer a quantity of Ak-Öl varying from 0, 0.75 to 0.98 g per gram prepolymer, respectively.

The reverse osmosis properties of these membranes were determined at room temperature and at a pressure of 40 bar in a solution comprising n-hexane with therein dissolved 1.0%, by weight, of n-docosane. The results are mentioned in table B.

Table B

Example	Non-reactive polymer Ak-Öl g/g prepolymer	n-Hexane flux l/m^2/h	Retention n-docosane
IXa	none	0	
IXb	0.75	27	72
IXc	0.98	52	71

From table B appears the favourable effect of the used non-reactive polymer on the flux.

Example X

The procedure of example I was repeated in the preparation of a series of composite membranes (Xa-Xd). The organic phase comprised toluene with therein dissolved 1.0%, by weight, of the prepolymer and as non-reactive polymer a quantity of Ak-Öl varying from 0, 0.25, 0.50 and 0.75 g per gram prepolymer, respectively.

The reverse osmosis properties of these membranes were determined at room temperature and at a pressure of 40 bar in a solution comprising toluene with therein dissolved 1.0%, by weight, of n-docosane. The results are mentioned in table C.

Table C

Example	Non-reactive polymer Ak-Öl g/g prepolymer	Toluene flux l/m^2/h	Retention n-docosane
Xa	none	17	84
Xb	0.25	45	85
Xc	0.50	49	80
Xd	0.75	68	77

From comparing the results of example X it appears that as the concentration of the non-reactive polymer Ak-Öl in the organic phase increases the toluene flux of the resulting membrane increases at nearly constant retention.

Example XI

An isocyanate determined prepolymer prepared from α,ω-bis(hydroxyl propyl)polydimethyl siloxane (OF 1025; Goldschmidt; M.W. 2185) and toluene diisocyanate (T-80) in a 1/2 molar ratio was used in a quantity of 1.24%, by weight, in the organic phase, namely: 1,1,2-trichloro trifluoro ethane (s.w. 1.575).

In the water phase 1%, by weight, of N4 (= N,N'-bis-(3-amino propyl ethylene diamine) was used.

As carrier membrane was used a polyimide type prepared from a 16%, by weight, solution (Lenzing P84) in DMF. Addition of 1 g poly-1-(trimethyl silyl)-1-propyne (PMSP) as non-reactive polymer per gram prepolymer in the organic phase led to modified measurement values for the pressure normalized N_2 and O_2 flux values of the composite membrane. The results are mentioned in table D.

Table D

Prepolymer %, by weight	Non-reactive polymer g/g prepolymer	N4 water phase %, by weight	Organic phase solvent	P/1 (N_2) mole/m^2.s.Pa (cm^3 [STP] / cm^2.s.cm Hg)	O_2/N_2
1,24	-	1,0	freon	$9,3.10^{-8}$ ($2,78.10^{-4}$)	2,20
1,24	1,0	1,0	toluene	$7,3.10^{-7}$ ($2,19.10^{-3}$)	1,60

Example XII

In an analogous manner as described in example I a composite membrane was prepared wherein in the water phase 0.2%, by weight, of $H_2N\text{-}CH_2CH_2CH_2\text{-}NH\text{-}CH_2CH_2\text{-}NH\text{-}CH_2CH_2CH_2\text{-}NH_2$, 0.05%, by weight, of poly(vinyl alcohol) (Mowiol 4-88^R, Hoechst) and 0.04%, by weight, of sodium dodecyl sulphate were used. The organic phase comprised toluene with therein dissolved 0.5%, by weight, of toluene diisocyanate (T-80, Bayer) and as non-reactive polymer 0.75 g of Ak-Öl per gram T-80.

The reverse osmosis properties of this membrane were determined at room temperature and at a pressure of 40 bar in a solution comprising toluene with therein dissolved 1.0%, by weight, of n-docosane with as result a toluene flux of 37 $l/m^2/h$ and a n-docosane retention of 63%.

Comparative Example XIIA

The procedure of example XII was repeated. The organic phase did not contain Ak-Öl. This membrane showed a toluene flux of 16 $l/m^2/h$ and a n-docosane retention of 33%.

From examples XII and XIIA appears the favourable influence of the non-reactive polymer on the flux and the retention.

Claims

1. A semi-permeable composite membrane with a porous carrier substrate whereon a polymer network obtained by interfacial polymerisation is applied, said network comprises an additional polymer, **characterized** in that said additional polymer which is a non-reactive and non-ionic polymer is dissolved in the water phase or in the organic phase, from which said interfacial polymerisation occurs, which additional polymer is molecularly entangled in said network and influences in particular the selectivity and the permeability of the composite membrane.

2. A semi-permeable composite membrane of claim 1, **characterized** in that the non-reactive (and non-ionic) polymer is a polyalkyl siloxane either branched or not with the formula

$$-(\underset{\displaystyle R_1}{\overset{\displaystyle R}{Si}} - O)-_n$$

wherein R and R_1 independent of each other represent a C_1-C_{20} alkyl or aryl group either substituted or not and n is an integral of 20-50.000 or a copolymer thereof.

3. A semi-permeable composite membrane of claim 2, **characterized** in that the polyalkyl siloxane is a polydimethyl siloxane with terminal trimethyl silyl groups.

4. A semi-permeable composite membrane of claim 1, **characterized** in that the non-reactive (and non-ionic) polymer is a polyacrylate or polymethacrylate with the formula

$$-(CH_2 - \underset{\displaystyle \underset{\displaystyle OR_3}{C=O}}{\overset{\displaystyle R_2}{C}} -)-_n$$

wherein R_2 = H or CH_3 and R_3 an alkyl either branched or not with 1-20 carbon atoms, while n is an integral of ≥ 10.

5. A semi-permeable composite membrane of claim 1, **characterized** in that the non-reactive (and non-ionic) polymer is a polyolefine either branched or not chosen from the group of polyisobutylene, polyisoprene or polybutadiene.

6. A semi-permeable composite membrane of claim 1, **characterized** in that the non-reactive (and non-ionic) polymer is a block copolymer of styrene-butadiene-styrene, styrene-isoprene-styrene, styrene-ethylene-butylene-styrene etc.

7. A semi-permeable composite membrane of claim 1, **characterized** in that the non-reactive (and non-ionic) polymer is cellulose acetate.

8. A semi-permeable composite membrane of claim 1, **characterized** in that the non-reactive (and non-ionic) polymer is a polyalkylene oxide, in particular polyethylene oxide with the formula $(CH_2\text{-}CH_2\text{-}O)_n$, wherein n is an integral of ≥ 20.

9. A semi-permeable composite membrane of claims 1-8, **characterized** in that the polymer regulating the membrane properties is present in the polymer network in a quantity of 5-90%, by weight, and preferably in a quantity of 10-60%, by weight, related to the total weight of the network.

10. A process for manufacturing a semi-permeable membrane by coating a porous substrate with a polymer network obtained by interfacial polymerisation, wherein the porous substrate is treated with a solution of at least one reactive polyfunctional monomer or oligomer or prepolymer with as reactive groups $-NHR_4$ (R_4 = H or alkyl with C_1-C_{20}), -OH or -SH and eventually a surfactant in water, whereafter the so treated substrate is further treated with a solution of at least one reactive polyfunctional monomer or oligomer or prepolymer or polymer with as reactive groups -COX, $-SO_2X$, $-POXR_5$, $-NR_6COX$ or -NCO, wherein X = Cl, Br or I, wherein R_5 and R_6 represent an alkoxy group or alkyl group with 1-16 carbon atoms, preferably 1-5 carbon atoms, in a suitable organic solvent, wherein a non-reactive and non-ionic polymer regulating the membrane properties according to claims 1-9 prior to the treatment of the substrate with the aqueous solution of the said reactive components is added in an amount of 5 - 90%, by weight, and preferably in an amount of 10 - 60%, by weight, related to the total weight of the network to that solution in case the polymer is soluble in water, whereas in case the polymer solves in an organic solvent, this is added to the organic solution of said reactive components, whereafter the so treated substrate is dried and is or is not subjected to a heat treatment, subsequently.

Patentansprüche

1. Eine semipermeable zusammengesetzte Membran mit einem porösen Trägersubstrat, auf das ein Polymernetzwerk, das durch eine Grenzflächenpolymerisation erhalten ist, aufgebracht ist, wobei das Netzwerk ein zusätzliches Polymer aufweist, dadurch gekennzeichnet, daß das zusätzliche Polymer, das ein nicht-reaktives und nicht-ionisches Polymer ist, in der Wasser-Phase oder in der organischen Phase aufgelöst ist, aus der die Grenzflächenpolymerisation stattfindet, wobei das zusätzliche Polymer in das Netzwerk molekular verwickelt ist und insbesondere die Selektivität und die Permeabilität der zusammengesetzten Membran beeinflußt.

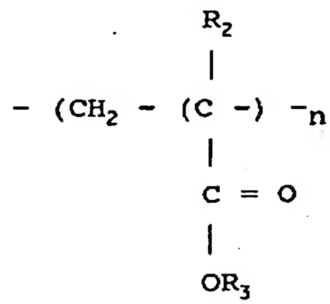
2. Eine semipermeable zusammengesetzte Membran gemäß Anspruch 1, dadurch gekennzeichnet, daß das nicht-reaktive und nicht-ionische Polymer ein verzweigtes oder nichtverzweigtes Polyalkyl-Siloxan mit folgender Formel ist:

$$-\!\left(\begin{array}{c} R \\ | \\ Si \\ | \\ R_1 \end{array} - O\right)\!-_n$$

wobei R und R_1 unabhängig voneinander eine C_1-C_{20}-Alkyl- oder-Aryl-Gruppe, die entweder substituiert oder nicht-substituiert ist, wobei n eine ganze Zahl von 20-50.000 ist, oder ein Copolymer derselben darstellen.

3. Eine semipermeable zusammengesetzte Membran gemäß Anspruch 2, dadurch gekennzeichnet, daß das Polyalkyl-Siloxan ein Polydimethyl-Siloxan mit End-Trimethyl-Silyl-Gruppen ist.

4. Eine semipermeable zusammengesetzte Membran gemäß Anspruch 1, dadurch gekennzeichnet, daß das nicht-reaktive und nicht-ionische Polymer ein Polyacrylat oder ein Polymethacrylat mit der Formel



ist, wobei R_2 = H oder CH_3 und R_3 ein entweder verzweigtes oder unverzweigtes Alkyl mit 1-20 Kohlenstoffatomen ist, während n eine ganze Zahl ≥ 10 ist.

5. Eine semipermeable zusammengesetzte Membran gemäß Anspruch 1, dadurch gekennzeichnet, daß das nicht-reaktive und nicht-ionische Polymer ein entweder verzweigtes oder nicht-verzweigtes Polyolefin ist, das aus der Gruppe aus Polyisobutylen, Polyisopren oder Polybutadien ausgewählt ist.

6. Eine semipermeable zusammengesetzte Membran gemäß Anspruch 1, dadurch gekennzeichnet, daß das nicht-reaktive und nicht-ionische Polymer ein Block-Copolymer aus Styren-Butadien-Styren, Styren-Isopren-Styren, Styren-Etylen-Butylen-Styren, usw. ist.

7. Eine semipermeable zusammengesetzte Membran gemäß Anspruch 1, dadurch gekennzeichnet, daß das nicht-reaktive und nicht-ionische Polymer Zellulose-Acetat ist.

8. Eine semipermeable zusammengesetzte Membran gemäß Anspruch 1, dadurch gekennzeichnet, daß das nicht-reaktive und nicht-ionische Polymer ein Polyalkylen-Oxid, insbesondere ein Polyetylen-Oxid mit der Formel $(CH_2-CH_2-O)_n$, wobei n eine ganze Zahl ≥ 20 ist, ist.

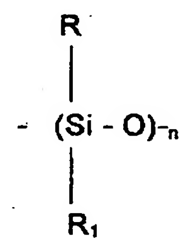
9. Eine semipermeable zusammengesetzte Membran gemäß einem der Ansprüche 1 - 8, dadurch gekennzeichnet, daß das Polymer, das die Membraneigenschaften regelt, in einer Menge von 5-90 Gewichtsprozent, und vorzugsweise in einer Menge von 10-60 Gewichtsprozent, bezogen auf das Gesamtgewicht des Netzwerks, in dem Polymernetzwerk vorliegt.

10. Ein verfahren zum Herstellen einer semipermeablen Membran durch das Beschichten eines porösen Substrats mit einem Polymernetzwerk, das durch eine Grenzflächenpolymerisation erhalten wird, bei dem das poröse Substrat mit einer Lösung aus zumindest einem reaktiven polyfunktionellen Monomer oder Oligomer oder Prepolymer mit $-NHR_4$ (R_4 = H oder Alkyl mit C_1-C_{20}), -OH oder -SH als reaktiven Gruppen und schließlich einem grenzflächenaktiven Stoff in Wasser behandelt wird, woraufhin das derart behandelte Substrat mit einer Lösung aus zumindest einem reaktiven polyfunktionellen Monomer oder Oligomer oder Prepolymer oder Polymer mit -COX, $-SO_2X$, $-POXR_5$, $-NR_6COX$ oder -NCO als reaktiven Gruppen weiterbehandelt wird, mit X = Cl, Br oder I, wobei R_5 und R_6 eine Alkoxygruppe oder eine Alkylgruppe mit 1-16 Kohlenstoffatomen, vorzugsweise 1-5 Kohlenstoffatomen, in einem geeigneten organischen Lösungsmittel darstellen, wobei ein nicht-reaktives und nicht-ionisches Polymer, das die Membraneigenschaften gemäß den Ansprüchen 1 - 9 regelt, vor der Behandlung des Substrats mit der wässrigen Lösung aus den reaktiven Komponenten in einer Menge von 5-90 Gewichtsprozent, und vorzugsweise in einer Menge von 10-60 Gewichtsprozent, bezogen auf das Gesamtgewicht des Netzwerks, der Lösung hinzugefügt wird, falls das Polymer in Wasser löslich ist, wohingegen, falls das Polymer in einem organischen Lösungsmittel löslich ist, dieses der organischen Lösung aus den reaktiven Komponenten hinzugefügt wird, woraufhin das so behandelte Substrat getrocknet und nachfolgend einer Wärmebehandlung unterzogen wird oder nicht.

Revendications

1. Membrane composite semi-perméable avec un substrat de support poreux sur lequel on applique un réseau de polymère obtenu par polymérisation interfaciale, ledit réseau comprenant un polymère supplémentaire, caractérisée en ce que le polymère supplémentaire, qui est un polymère non réactif et non ionique, est dissout dans la phase aqueuse ou dans la phase organique, à partir de laquelle ladite polymérisation interfaciale survient, ce polymère supplémentaire est enchevêtré moléculairement dans ledit réseau et exerce une influence en particulier sur la sélectivité et sur la perméabilité de la membrane composite.

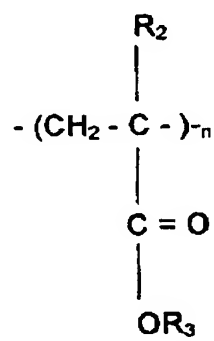
2. Membrane composite semi-perméable selon la revendication 1, caractérisée en ce que le polymère non réactif et non ionique, est un polyalkyl siloxane ramifié ou non ayant pour formule



dans laquelle R et R_1, indépendamment l'un de l'autre, représentent un groupement en C_1-C_{20} alkyle ou aryle, substitué ou non, et n est en cela un nombre entier de 20 à 50 000
ou un copolymère de celui-ci.

3. Membrane composite semi-perméable selon la revendication 2, caractérisée en ce que le polyalkyl siloxane est un polydiméthyl siloxane ayant des groupements terminaux triméthyl silyle.

4. Membrane composite semi-perméable selon la revendication 1, caractérisée en ce que le polymère non réactif et non ionique est un polyacrylate ou un polyméthacrylate ayant pour formule :



dans laquelle R_2 = H ou CH_3, et R_3 un alkyle ramifié ou non, ayant de 1 à 20 atomes de carbone, tandis que n est un nombre entier de valeur ≥ 10.

5. Membrane composite semi-perméable selon la revendication 1, caractérisée en ce que le polymère non réactif et non ionique est une polyoléfine ramifiée ou non, choisie dans le groupe du polyisobutylène, du polyisoprène et du polybutadiène.

6. Membrane composite semi-perméable selon la revendication 1, caractérisée en ce que le polymère non réactif et non ionique est un copolymère en blocs styrène-butadiène-styrène, styrène-isoprène-styrène, styrène-éthylène-butylène-styrène, etc.

7. Membrane composite semi-perméable selon la revendication 1, caractérisée en ce que le polymère non réactif et non ionique est de l'acétate de cellulose.

8. Membrane composite semi-perméable selon la revendication 1, caractérisée en ce que le polymère non réactif et non ionique est un oxyde de polyalkylène, en particulier un oxyde de polyéthylène ayant pour formule $(CH_2-CH_2-O)_n$, dans laquelle n est un nombre entier de valeur ≥ 20.

9. Membrane composite semi-perméable selon les revendications 1 à 8, caractérisée en ce que le polymère qui régule les propriétés de la membrane est présent dans le réseau de polymère en une quantité de 5 à 90 %, en poids, et de préférence en une quantité de 10 à 60 %, en poids, par rapport au poids total du réseau.

10. Procédé de fabrication d'une membrane composite semi-perméable en enrobant un substrat poreux avec un réseau de polymère obtenu par polymérisation interfaciale, dans lequel on traite le substrat poreux avec une solution d'au moins un monomère ou un oligomère ou un prépolymère polyfonctionnel réactif ayant des groupements réactifs $-NHR_4$ (R_4 = H ou un alkyle avec (C_1-C_{20}), -OH ou -SH) et éventuellement un agent tensio-actif, dans l'eau, après quoi on traite le substrat ainsi traité avec une solution d'au moins un monomère ou un oligomère ou un prépolymère ou un polymère polyfonctionnel réactif ayant comme groupements réactifs -COX, $-SO_2X$, $POXR_5$, $-NR_6COX$ ou -NCO, dans lesquels X = Cl, Br ou I; dans lesquels R_5 et R_6 représentent un groupement alkoxy ou un groupement alkyle avec 1 à 16 atomes de carbone, de préférence 1 à 5 atomes de carbone, dans un solvant organique approprié, dans lequel un polymère non réactif et non ionique qui régule les propriétés de la membrane selon les revendications 1 à 9, est ajouté, préalablement au traitement du substrat, à la solution aqueuse desdits composés réactifs en une quantité de 5 à 90 %, en poids, et de préférence en une quantité de 10 à 60 %, en poids, par rapport au poids total du réseau au cas où le polymère est soluble dans l'eau, alors qu'au cas où le polymère se dissout dans un solvant organique, celui-ci est ajouté à la solution organique desdits composés réactifs, après quoi on sèche le substrat ainsi traité et, par la suite, on le soumet ou non à un traitement par chauffage.